Northeastern University

On the fly EIS tracking of rechargeable alkaline Zn-MnO₂ batteries for large-scale use

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Alkaline Zn-MnO₂

- Zn and MnO₂ are high-capacity materials
 - Zn: **817 mAh/g** (2-electron)
 - MnO₂: **617 mAh/g** (2-electron)
- Aqueous: lower potential than Li-ion (organic)
 - 1.5 V nominal

For the grid: Cost and safety are main drivers

Engineering a deep-cycled MnO₂ electrode

- Zinc depth of discharge (DOD)
- MnO₂ cathode mass loading

Grid Storage Requirements[†]

T&D Upgrade Deferral
(50th Percentile)
3-6 h discharge, \$584/kW benefit

Wind Grid Integration
1-6 h discharge, \$441/kW benefit

Renewables Load Shift
3-5 h discharge, \$311/kW benefit

Demand Charge Management
5-11 h discharge, \$582/kW benefit

Transmission Congestion Relief
3-6 h discharge, \$86/kW benefit

[†] J. Eyer, G. Corey, Sandia
report, SAND2010-0815, 2010.

Primary Zn-MnO₂

Shallow-cycle Zn-MnO₂ battery results

Electrochemical systems	Cycle life (cycles)	Capital cost (\$ per kWh)	Efficiency (% , average)	Lifetime investment cost (¢ per kWh per cycle)	Notes
Pb-acid	500–1000	200–400	75	27–107	Lead toxicity
Ni–Cd	2000–2500	800–1500	65	49–115	Cadmium toxicity
Na–S	2500	300–500	82.5	15–24	High temperature, Safety issues
V-redox	12,000	150–1000	80	2–10	Poor energy-to-volume ratio
Li-ion (various)	1000–10,000	600–2500	92.5	7–270	Safety issues
ZEBRA	2500	100–200	87.5	5–9	High temperature
Zn–Br	200	150–1000	67.5	11–74	Bromine toxicity
Zn–MnO ₂	3200	140 (at 10% DOD) 90 (at 20% DOD) ^a	80–85	3 ^b –5	Aqueous chemistry, non-toxic

^a Current testing indicates cycle life >550 at the time of writing.

^b Based on projected cycle life of 2000 at 20% DOD.

Large-format shallow-cycled Zn-MnO₂

95 Ah UEP Generation 1
3 in × 6 in electrode size
11 cathodes, 12 anodes

Cycling protocol and DEV as a SOH metric

CCCV cycling

62 mAh/g-MnO₂ (20% DOD, 1e⁻)

Why use EIS?

Electrochemical Impedance Spectroscopy

+ Physically & chemically significant model

Electrode spot testing during production:

Quality control tool. Production troubleshooting with mechanistic understanding.

On the fly tracking during cycling:

1. EIS tracking of test cells connects performance to phenomena
2. Results can be used to train control systems based on cheaper tests, via machine learning

On the fly EIS monitoring protocol

Initial EIS

Loop:

Loop: Repeat n-1 times

CC Discharge

OCV

CC Charge to limit

CV Charge to cutoff current

OCV

CC Discharge

OCV

Discharged EIS

CC Charge to limit

CV Charge to cutoff current

OCV

Charged EIS

n-1 cycles

nth cycle with EIS

n = 5 or 10

On the fly EIS: Charged state

But:
More interesting to know about the
electrodes individually

Scaled-down cell for EIS tracking

Scaled-down UEP Generation 1

(S2 box)

2 in × 5 in electrode size

2 cathodes, 3 anodes

5-6 Ah cycled capacity

cathode type 1: 0.9 mm thickness

cathode type 2: 1.0 mm thickness

Tracking

Luggin placement

All Cathode type 1 cells

Charged

Discharged

Porous electrode full-cell model

Based on Donne, *Journal of The Electrochemical Society*, 153 (7) A1332-A1340 (2006)

(a) Cathode interfacial model

(b) Anode interfacial model

Modification of Hampson and McNeil, *Journal of Power Sources*, 15 (1985) 61-76

Porous electrode model

Porous electrode full-cell model

Cathode interfacial model (charged)	$Z_i = \frac{R_1}{j\omega R_1 C_1 + 1} + \frac{j\omega L_2 R_2}{(j\omega)^2 C_2 L_2 R_2 + j\omega L_2 + R_2} + \frac{A_3}{\sqrt{j\omega}}$
Cathode interfacial model (discharged)	$Z_i = \frac{R_1}{j\omega R_1 C_1 + 1} + \frac{j\omega L_2 R_2}{(j\omega)^2 C_2 L_2 R_2 + j\omega L_2 + R_2} + \frac{Q_3}{(j\omega)^{a3}}$
Anode interfacial model	$Z_i = \frac{j\omega L_1 R_1}{(j\omega)^2 C_1 L_1 R_1 + j\omega L_1 + R_1} + \frac{Q_2}{(j\omega)^{a2}}$
Porous electrode model	$Z = R_{inf} + \sqrt{R_e Z_i} \coth \left(\ell \sqrt{\frac{R_e}{Z_i}} \right)$

Model fitting results: Cathode type 1

Cathode type 1: **Charged**

Cathode type 1: **Discharged**

Circles: experimental data
Small squares: model fit

Model fitting results: Cathode type 1

Cathode only

(Obvious question: is this an artefact?)

Circles: experimental data
Small squares: model fit

Model fitting results: Cathode type 2

Cathode type 2: **Charged**

Cathode type 2: **Discharged**

Circles: experimental data
Small squares: model fit

Cell
Cathode
Anode

Cell
Cathode
Anode

Model fitting results

Cathode type 2

1. High resistance at surface sites by cycle 15.
2. No variation in pore inductance with SOC.
3. Rising resistance at the pore level.

Lumped parameters: RC time constant

Cathode Model Circuit

Lumped parameters: Quality factor

Cathode Model Circuit

$$Q = R \sqrt{\frac{C}{L}}$$

Expectations for a 1/1 + symmetric cell

Thank you

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U.S. DEPARTMENT OF
ENERGY

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IR UV X

Setup

EIS tracking strategy

Cathodes: charged

Cathodes: discharged

Anodes: charged

Anodes: discharged

Li-ion cost—Argonne National Lab

The irreversible threshold

Material in cells tested (Duracell AA):

$P_r = 0.39$

Fraction pyrolusite (1×1) slabs

$x_2 = 0.76$

Fraction ramsdellite (2×1) capacity

CCNY Tronox:

$P_r = 0.40$

Fraction pyrolusite (1×1) slabs

$x_2 = 0.75$

Fraction ramsdellite (2×1) capacity

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Most important attributes
for stationary, grid-scale
storage